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SPECTROCHEMICAL PRECISION STUDIES WITH THE VACUUM-CUP ELECTRODE

Part I - Calcium, Magnesium, Phosphorus and Potassium

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ABSTRACT

Lack of precision in solution analysis using a commercially available graphite vacuum-cup electrode was attributed to varying porosity in graphite. Substitution of the graphite electrode by a non-porous silver electrode produced a marked increase in precision.

INTRODUCTION

The purpose of this study was to compare direct-recording spectrometry and photographic recording in solution spark analysis. The Pulp and Paper Research Institute of Canada had undertaken a photographic study while the spectrochemical laboratory of the Mines Branch undertook a direct-recording spectrometric study. A rotating disc electrode assembly

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was used for the photographic study. Because this assembly was not available for the direct-reading instrument it was replaced by a vacuum-cup electrode. The essential difference between the two electrode arrangements is that the solution is carried to the excitation column by a rotating disc in one case, and lifted through an electrode channel by a vacuum effect in the other.

A graphite, vacuum-cup electrode was used for the initial part of the study. This type of vacuum-cup electrode has been used by several authors (2, 3, 4, 5) but little information appears to have been published on its precision capabilities. The results obtained by the authors of this paper with this type of electrode were poor, even though attempts were made to improve the precision with known aids (5, 6). The variation in porosity, from electrode to electrode, appears to be the principal disadvantage of the graphite vacuum-cup electrode.

The removal of the porosity effect by the substitution of a silver vacuum-cup-electrode system improved the precision markedly. Although metallic vacuum-cup electrodes have been used (2, 7), little information is available on the resulting analytical precision. The principal advantage of the silver-electrode system is the absence of the porosity effect. The disadvantage is the limitations imposed by its chemical properties.

HISTORICAL DEVELOPMENT OF THE VACUUM-CUP ELECTRODE

Eichoff and Picard (7) are the first authors to describe and apply an elementary form of the vacuum-cup electrode. A precision of 5 to 10% with a copper electrode system for the determination of the alkali metals was reported.

S. L. Mandelstaam (1) investigated the mechanism of the spark-channel formation in a discharge tube. He found that the discharge pressure wave removes the gases from the axial region of the spark canal creating a plasma of very low gas density or, in other words, a vacuum. This phenomenon applies to the discharge in an analytical gap as well, except that the geometrical arrangement is spherical rather than cylindrical. The vacuum created by the pressure wave, in the case of the vacuum-cup-electrode system, lifts the solution into the excitation column. The rate at which the sample is transferred from the Teflon cup to the excitation column is dependent upon the diameter of the electrode channel and the number of discharges per half cycle.

After the appearance of Eichoff and Picard's paper, similar electrode systems have been described in the literature (8, 9, 10), but lacking an electrode channel, the sample transfer mechanism is by capillary diffusion.

T. H. Zink (2) used both metallic and graphite electrodes, although the results reported were obtained with the graphite electrode. He quotes a precision of 4% in determining zirconium at the 50 ppm level in a bismuth-uranium alloy. He encountered considerable shifting of the working curves from day to day, a distinct disadvantage in direct-recording spectrometry.

A method of overcoming the varying porosity effect of the graphite electrode has been suggested (5) but is time-consuming. This technique involves soaking the electrode in the solution to be analyzed, discarding the first two exposures and recording the next eight to ten exposures. On the other hand,

the porosity effect of the graphite electrode has been used to advantage for the analysis of small amounts of solution (11). The electrode channel is packed with graphite and thus acts as a wick.

An extension of the vacuum-cup electrode is the stick electrode (2, 3). The stick electrode is made by drilling an axial channel in a rod of conducting material. The lower end of the rod is immersed in the solution in a vessel below the electrode jaws. This arrangement does not require a Teflon cup and thus eliminates the possibility of transfer contamination by using the vessel in which the solution is prepared.

APPARATUS

Excitation Source:	Baird-Atomic Spectrosource
Spectrograph:	Jarrell-Ash 3.4 metre Ebert mounting instrument, equipped with a digital integrator system.

PROCEDURE

Standard Solutions: The solutions were prepared by the Pulp and Paper Research Institute of Canada. The composition of the solutions is given in Table 1.

TABLE 1

Compositions of Solutions

Element	Solution XXXMXT	Solution XXMXT	Solution XVMXT
Co	0.04%	0.04%	0.04%
K	3.10	1.80	1.20
Ca	2.30	1.50	1.00
Mg	0.90	0.50	0.20
P	1.01	0.68	0.47

Electrode System - The silver vacuum-cup electrode was made by the Mines Branch Technical Services Division, from a one-quarter-inch Johnson-Matthey Specpure silver rod. The dimensions of the electrode are identical to the commercially available graphite vacuum-cup electrode, listed as electrode number 6011 in the Ultra Carbon Corporation catalogue of December 1964. The important dimensions of this electrode are:

vertical channel diameter	0.79 mm
vertical channel length	18.13 mm
horizontal channel diameter	1.60 mm
length of vertical channel above solution,	9.53 mm

The silver vacuum-cup electrode with a Teflon cup formed the lower electrode assembly. A one-quarter-inch silver rod served as the upper electrode. The counter electrode was machined to a 120-degree cone before the analysis.

A syringe, with a precision of better than one per cent, was used to dispense 1.50 ml. of solution into the Teflon cup. This amount of solution filled the cup. The reason for filling the cup is that the large amount of solution in the cup minimizes the change in effective capillary height during operation.

About half a millilitre was consumed during each exposure. The remaining solution in the cup was discarded. Between replicates, the electrode and cup were rinsed with 1.20 hydrochloric acid, distilled water and acetone.

Excitation

High voltage a-c spark	nominal 30 kV
Inductance (microhenries)	10
Capacitance (microfarad)	0.005
Resistance	residual
Spark current (r.f.amps.)	10
Discharges/half cycle	ca. 12
Spark current control, dial setting	55
Analytical gap (mm)	4
Auxiliary gap (mm)	1.5

Exposure

Entrance slit width (microns)	25
Exit slit widths (microns)	50
(except for Cs 4555.36A, which was 75 microns)	
Spark preburn (sec.)	15
Spark exposure	controlled by Co 3409.18A

TABLE 2

Analytical Lines

Element	Analytical Line	Internal Standard Line
K	4044.14A	
Ca	3644.41	Co 3409.18
Mg	2779.83	
P	2535.65	

RESULTS

The results of the study are indicated in Table 3. The figures given are the results of 32 replications. Corrections for background were not applied. The standard deviation and coefficient of variance were calculated in accordance with ASTM suggested practises for use of statistical methods in spectrochemical analysis (12).

A constant illumination by a light pipe immediately in front of the photomultiplier tubes was used for the spectrometer precision test. The results in Table 4 represent 32 replications.

TABLE 3

Results of Study

Element	Solution XXXMXT			
	%	Mean	S. D.	C. V.
Potassium	3.10	566.8	49.6	8.8
Calcium	2.30	1719.6	51.3	3.0
Magnesium	0.90	733.2	60.6	8.3
Phosphorus	1.01	1085.1	62.1	5.7
Background at 4555A	-	1088.9	30.8	2.8
Exposure time, seconds	-	32.3	3.93	12.1

Element	Solution XXMXT			
	%	Mean	S. D.	C. V.
Potassium	1.80	423.9	13.5	3.2
Calcium	1.50	1403.8	20.8	1.5
Magnesium	0.50	507.8	24.1	4.7
Phosphorus	0.68	1027.5	24.0	2.3
Background at 4555A	-	1010.7	23.3	2.3
Exposure time, seconds	-	25.6	0.878	3.4

Element	Solution XVMXT			
	%	Mean	S. D.	C. V.
Potassium	1.20	369.5	13.2	7.8
Calcium	1.00	1168.0	22.9	2.0
Magnesium	0.20	305.2	18.3	6.0
Phosphorus	0.47	951.0	28.2	3.0
Background at 4555A	-	945.5	29.6	3.1
Exposure time, seconds	-	24.6	0.871	3.5

TABLE 4

Spectrometer Precision Check

Channel	Element	Mean	S.D.	C.V.
1	Potassium	552.3	3.9	0.7
2	Calcium	539.8	4.2	0.8
3	Magnesium	501.8	1.6	0.3
4	Phosphorus	423.1	3.5	0.8
5	Background at 4555A	270.8	2.3	0.8

DISCUSSION

The exit slit at 4555.36 A was installed to monitor cesium. A spectroscopic buffer, cesium chloride, was added to a portion of solution XXXMXT in an attempt to improve the precision of the graphite vacuum-cup-electrode system. This did not have the desired effect and the line was used to monitor background in subsequent exposures.

The coefficient of variance of the exposure time for solution XXXMXT is greater than for the other two solutions. During the replication of solution XXXMXT, it was observed that there was a progressive decrease in exposure time which coincided with a deterioration of the counter electrode cone. Rather than machine a fresh cone on the counter electrode, it was left with the shape it had assumed after 32 exposures. This resulted in a more-consistent exposure time for the remaining solutions.

The coefficient of variance of the elements is at a minimum for solution XXMXT. It would appear that this can be attributed to an optimum

concentration for the spectroscopic system and the spectrometer controls, rather than to a change in the silver vacuum-cup electrode due to wear. The similar exposure time and exposure time coefficient of variance of solutions XXMXT and XVMXT indicate a stabilization of the electrode system.

A distilled water exposure, under direct recording spectrometric conditions, prompted the photographic recording of solution XXXMXT and distilled water. The spectrometric recording of the distilled water exposure produced counts which were less than the counts produced by the weakest solution, except for potassium. An examination of the photographic plate revealed that the background from the wings of the silver line at 4055.26 A appeared to be greater for a distilled water exposure than for the exposure of solution XXXMXT. Presumably the same phenomenon occurs under direct-recording spectrometry, and can be readily explained by the lack of metallic ions, other than silver, in the excitation column. The result is an enhancement of the silver radiation in a distilled water exposure as compared with an exposure from an analytical solution.

The counts obtained from the distilled water exposure for calcium, magnesium and phosphorus, under direct-recording-spectrometric conditions, are very close to the zero intercept of Figures 2, 3, and 4.

Gold is a promising material for a metallic vacuum-cup electrode. The advantage of such an electrode lies in being able to work with several acids without suffering electrode attack. The disadvantage is the expense but it

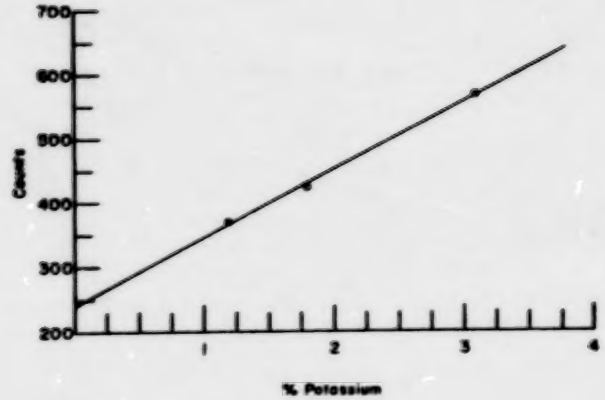

Figure 1 - Working curve for potassium

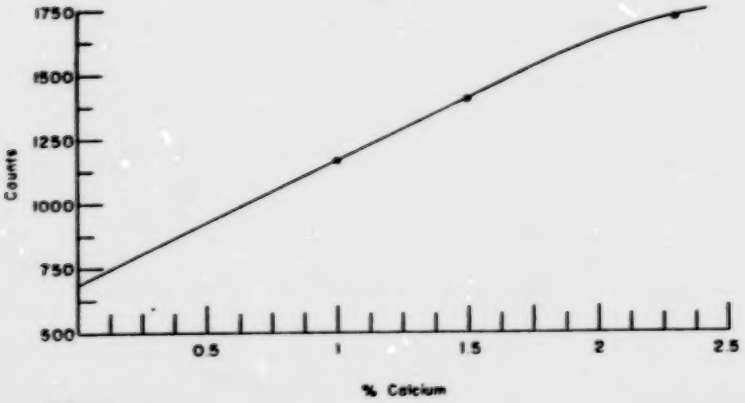

Figure 2 - Working curve for calcium

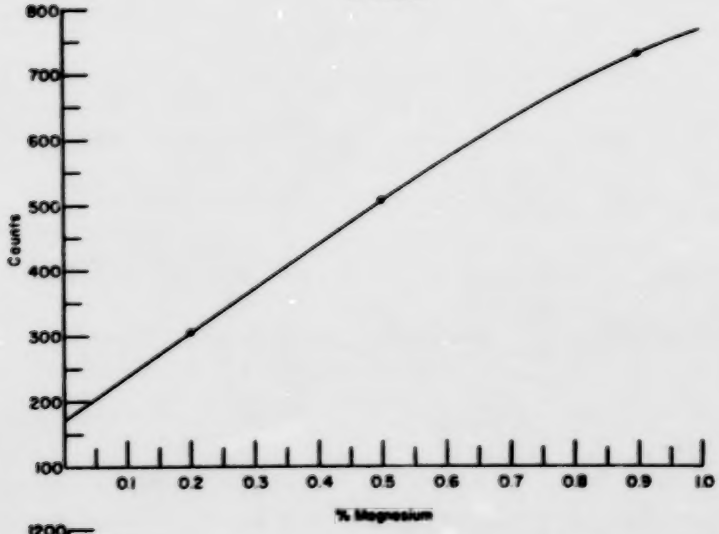

Figure 3 - Working curve for magnesium

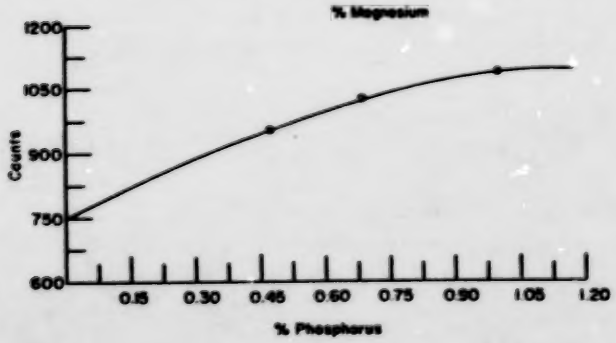

Figure 4 - Working curve for phosphorus

should be possible to use other materials for the base and gold for the axial channel portion.

SUMMARY

The graphite vacuum-cup-electrode system was abandoned because of lack of precision which was attributed to varying porosity. The silver vacuum-cup-electrode system produced an acceptable precision for a spark method.

The precision ranged from a high of 8.8 per cent for potassium at the high concentration to a low of 1.5 per cent for magnesium at the intermediate concentration. Most of the coefficients of variation were less than 5 per cent.

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